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Dynamics and Rheology of Supercooled Liquids

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A number of MD simulations have detected mobile clusters or strings in coexistence with immobile regions in supercooled model binary mixtures with various visualization methods. This suggests that rearrangements of particle configurations in glassy materials are cooperative, involving many molecules. We have introduced *bond breakage* among adjacent particle pairs and obtained the correlation length ξ of the clusters. Note that ξ measures a characteristic size of the active region where cooperative motions with string-like objects are aggregating, so it may grow up to a macroscopic scale as T is lowered. On the other hand, experiments have shown that the diffusion constant D of a tagged particle in a supercooled liquid is considerably larger than that predicted by the Einstein-Stokes relation. The same tendency has been confirmed by MD simulations. The origin of this phenomena is now ascribed to coexistence of relatively active and inactive regions among which the diffusion constant varies significantly. To study these aspects with less ambiguity, we have studied the kinetic heterogeneity in the particle diffusivity, which is essentially the same as that in the bond breakage.

As another interesting direction in this field, we stress the importance of nonlinear, nonequilibrium processes such as aging effects and nonlinear rheology in supercooled liquids. We studied the latter problem and found that externally applied shear rate $\dot{\gamma}$ induces jump motions or bond breakage when $\dot{\gamma}$ exceeds the inverse α relaxation time. Under shear, we have obtained a simple formula for the structural relaxation rate

$$\tau_\alpha(T,\dot{\gamma})^{-1} = \tau_\alpha(T,0)^{-1} + const.\dot{\gamma}, \tag{1}$$

and a dynamical scaling relation

$$\eta - \eta_B \sim \tau_\alpha \sim \xi^z, \tag{2}$$

where η and η_B are the total and a small background viscosities. These simple relations hold well for any T and $\dot{\gamma}$ covered in our simulations with $z = 4$ in 2D and 2 in 3D. It is remarkable that ξ (and τ_α) decreases with increasing $\dot{\gamma}$, so $\dot{\gamma}$ plays a role similar to a magnetic field in Ising systems near the critical point.

Molecular dynamics simulations are performed also for a polymer melt composed of short chains in quiescent and sheared conditions. In supercooled states where glassy component of the stress is pronounced, the stress relaxation function $G(t)$ exhibits a stretched exponential decay in a relatively early stage and ultimately follows the Rouse function $G_R(t)$. Transient stress evolutions after applications of shear thus obey the linear growth $\int_0^t dt'G(t')$ for strain less than 0.1 and then saturates into a non-Newtonian steady state value. This initial growth is much steeper than the Rouse growth $\int_0^t dt'G_R(t')$ for which the stress-optical relation holds. Elongation of chains into ellipsoidal conformations is found in shear flow as for the Rouse model. However, the elongation saturates into a limiting amount upon increasing the shear rate giving rise to a strong shear-thinning non-Newtonian behavior at extremely small shear rate on the order of the inverse Rouse time.

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